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LONG-RANGE OBJECTIVES

The long range objective of this project is to use the fluorescence of dissolved organic matter (DOM) as a unique investigative tool for studying biological, chemical and physical processes in the ocean. These processes include production of new marine dissolved organic carbon (DOC) by producers and grazers, mixing between marine and fresh waters, upwelling, downward mixing, transport of new production out of the euphotic zone as DOC, and transformation of dissolved organic carbon pools in the ocean. The high resolution data obtained from excitation-emission matrix spectroscopy (EEMS) also provide the detailed spectral information on gelbstoff absorption and fluorescence required for development of radiative transfer models.

SCIENTIFIC OBJECTIVES

Our short-term objectives are 1) to measure fluorescence and absorption properties of DOM in a wide variety of marine, estuarine, and terrestrial samples, 2) to determine variability in DOM optical properties as a function of physical, chemical and biological variables, and 3) to improve data acquisition rates.

APPROACH

High resolution fluorescence spectroscopic analyses, consisting of a series of emission spectra collected at forty individual excitation wavelengths, are combined with measurements of hydrographic parameters, chlorophyll and DOC concentrations, and UV-

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13. ABSTRACT (Maximum 200 words)
Our results to date have provided proof of concept for application of EEMS to ocean chemistry, biology, optics, and tracer studies. EEMS has provided new insight into the chemical composition of DOM in natural waters. Fluorescence spectroscopy can provide a rapid, underway, real-time method for distinguishing between various pools of DOC and to look for transport of newly-formed DOC Out of the euphotic zone. Analysis is rapid enough to permit sampling at spacial resolution similar to that of other hydrogrpahic parametiers, such as nutrients. This gives us the ability to for the first time to incorporate DOC compositional information into large scale circulation models, thereby increasing our understanding of DOC cycling in the ocean and providing new insights into pathways, sites, and rates of DOC transformation. Elaboration of differences in spectral properties due to gelbstoff source and the conditions under with measurements are made should also lead to improvement of radiative transfer models.

The linear relationship between CDOM fluorescence and salinity could provide an optical tracer amenable to remote sensing techniques using passive or active sensors. Passive sensors have been used successfully to produce surface salinity maps from AVIRIS data based on gelbstoff absorption (Carder et al. 1993). Data of this type could be extremely useful in coastal waters where remote sensing generated surface temperature maps alone do not permit *extrapolation of water mass distribution and mixing.

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visible absorption spectra for water samples from a wide range of natural environments. Results are examined for evidence of differences in DOM spectral properties attributable to processes such as new marine production, photodegradation, biological utilization, and water mass mixing. Characterization of spectral variability due to the influence of multiple sources and sinks may help to explain the non-linearities sometimes observed in the salinity:DOM fluorescence or DOM fluorescence:DOC concentration relationships and thereby improve freshwater mixing models in coastal regions.

TASKS COMPLETED

We have analyzed hundreds of samples from sites throughout the world, including several major river systems. The fluorescence fingerprints obtained from excitation-emission analysis provide a library of water mass types based on DOM composition.

The usefulness of DOM fluorescence as a conservative water mass tracer even at full seawater salinities has been demonstrated in the Gulf of Mexico and the Gulf of Maine using both discrete samples and in situ instrumentation.

Data acquisition times have been decreased by a factor of 5-10 using a liquid nitrogen-cooled charge coupled device (CCD) array detection system. Individual emission scans can be collected in 1 - 30 sec, depending on DOM concentration in the samples.

RESULTS

In the past two years, our application of EEMS has yielded important new information regarding DOM concentration, composition, and optical properties which is unobtainable in any other way, since other analyses either require preconcentration or lack the necessary sensitivity or resolution. The three major overall findings can be summarized as:

1. Both emission and excitation maxima of marine humic material is blue-shifted relative to terrestrial humic material. This supports the conclusions from chemical analyses that marine humics are structurally distinct and may be formed *in situ*. Gelbstoff from different sources can be distinguished using EEMS, thereby extending the utility of fluorescence as a tracer into areas where multiple fluorescence sources are present.

2. A protein-like fluorescence signal, associated with biological activity, shows a distribution which is uncoupled from that of gelbstoff. It may serve as a tracer of new, labile DOC from areas of high productivity or organic-rich porewaters. Its strong absorption below 300 nm and fluorescence in the UV-A range have important implications for oceanic biology and optics.

3. Fluorescence intensities for water samples from different origins can be seriously underestimated (by up to 40%) depending on which wavelengths are used for excitation

and emission. This has important implications in the development of models to predict optical properties of seawater.

4. We have successfully deployed in situ instrumentation for colored DOM (CDOM) fluorescence measurements on moorings in Tampa Bay and 50 miles offshore in the Gulf of Mexico. Our preliminary results show adequate dynamic range and stability to easily resolve differences of less than 0.2 psu at salinities of 30 - 34.5 psu over time periods of days to months (Coble and Weisberg, unpublished).

The instrument we used was a SeaTech fluorometer modified for DOM fluorescence (Ex = 300-350 nm; Em = 430-480 nm). Results from an 11-day deployment in Tampa Bay show DOM fluorescence and salinity were highly correlated with least squares regression coefficients for 48-hour intervals of 0.99. Slopes and intercepts decreased during the deployment period, perhaps reflecting rainfall or additional river input from two major storms which passed through during the study period. Maximum and minimum salinities decreased by 0.5 ppt, lending support to this hypothesis. Neither chlorophyll **a** nor temperature were correlated with either salinity or DOM fluorescence. The salinities observed during the second deployment in the Gulf of Mexico ranged from 33.65 to 34.9 psu, and again the CDOM fluorescence signal was large and highly correlated with physical mixing processes as observed by T-S properties and ADCP current meter data (R. Weisberg, personal communication).

These results indicate that measurements of CDOM optical properties are sensitive enough and conservative over sufficiently long time periods to be useful in identification of microstructure formation processes. The additional information which can be obtained from spectral fluorescence and absorption measurements should permit us to separate conservative and non-conservative species of CDOM and further improve CDOM-salinity correlation in coastal regions.

IMPACT FOR SCIENCE

Our results to date have provided proof of concept for application of EEMS to ocean chemistry, biology, optics, and tracer studies. EEMS has provided new insight into the chemical composition of DOM in natural waters. Fluorescence spectroscopy can provide a rapid, underway, real-time method for distinguishing between various pools of DOC and to look for transport of newly-formed DOC out of the euphotic zone. Analysis is rapid enough to permit sampling at spatial resolution similar to that of other hydrographic parameters, such as nutrients. This gives us the ability for the first time to incorporate DOC compositional information into large scale circulation models, thereby increasing our understanding of DOC cycling in the ocean and providing new insights into pathways, sites, and rates of DOC transformation. Elaboration of differences in spectral properties due to gelbstoff source and the conditions under which measurements are made should also lead to improvement of radiative transfer models.

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RELATIONSHIPS TO OTHER PROGRAMS OR PROJECTS

We have collaborated with numerous other investigators on projects funded by ONR, NSF, NASA, NRL, MMS, and NOAA. Gulf of Mexico cruises were in conjunction with Carder and Muller-Karger (USF, NASA funding) and Weidemann (NRL). Additional Gulf of Mexico samples were provided by Benner (UT, NOAA NECOP project) and Means (LSU, MMS LATEX project). Columbia River project was in collaboration with Prahl (OSU, NSF LMER funding). Analysis of samples from the equatorial Pacific Ocean was made possible by Hedges (UW), Benner (UT), Peltzer (WHOI) and Hoge (WFF) with funding from NSF JGOFS. Amazon River samples were collected by Hedges (UW, NSF CAMREX project). Gulf of Maine samples were analyzed in collaboration with Perry and Roesler (UW, ONR MLML project). NSF REU program supported undergraduate research projects for three students during summer 1991 and 1992. This research also completed my own NSF project (#OCE-9116497).

Past results and findings will be applied to two additional projects on which I am a P.I.: the upcoming ONR ARI on Coastal Optics and Mixing, and an ONR-funded sensor development project currently underway at USF.

STATISTICAL INFORMATION

Publications:

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Graduate students: R. Michael Swaine

Patents: 0

Invited Lectures

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Manuscripts in preparation:

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Swaine, R.M. Characterization of colored dissolved organic matter using HPLC. M.S. Thesis. Univ. South Florida.

Coble, P.G. and R. Keil. Dissolved fluorescence, DCAA, and DFAA concentrations in the North Pacific Ocean.

Coble, P.G., M.L. Wells, and I. Koike. Molecular weight and fluorescence of colloidal particles in seawater.

Coble, P.G., and L.M. Mayer. Distribution and spectral characterization of fluorescent DOM in coastal regions.